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DIELECTRIC ANALYSIS OF AN EPOXY PREIMPREGNATED MATERIAL

PDO 6989221, Final Report

J. M. Walker, Project Leader

Project Team:
R. P. Hyer
F. E. Meisner

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The introduction to the principles of dielectric analysis as it relates to the cure mechanism of a preimpregnated material is given. The relationship between dielectric behavior and polymer response is also discussed. Dissipation versus time and temperature curves are presented and their relationship to production cycles and extent of cure analysis is shown.

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CONTENTS

ILLUSTRATIONS

TABLE

SUMMARY

Preimpregnated materials (prepregs) are difficult to characterize because they are constantly changing as a result of being only partially cured. To compensate for these changes, the time, temperature, and pressure requirements of the cure cycles are vague and provide maximum flexibility to the processor. This flexibility results in trial and error processing and inspection of the prepreg and a consistently high scrap rate. Most methods for analyzing a polymer require special specimens and are destructive. Dielectric analysis is a procedure that has potential because it is nondestructive and can be adapted to various specimen types. Dielectric analysis is based on the response of the dipoles within a polymer to an alternating electric field. Capacitance is the ability of the dipoles to align and dissipation is the power lost in attempting to align. Both are affected by viscosity, molecular weight, and the frequency of the alternating field. Thermoplastic polymers have the simplest response while the thermosets are more complex because of the cure mechanism.

The equipment chosen for this study was the Audrey II, System 300 dielectric analyzer coupled with an additional recorder, an oscilloscope, and a laboratory press. Three electrode designs allow the Audrey to monitor resins on a glass fabric carrier, resins with conductive reinforcement, and polymerizations or resin cooks. The System 300 consists of a test cell, a temperature controller, a card type programmer, and a recorder. Outputs are given in dissipation and capacitance as functions of time, temperature, and frequency. For a thermoset material, dissipation versus time curves show the cure mechanism and can be related to chemical and physical changes. Dissipation versus temperature curves can be used to obtain extent of cure information by monitoring the hysteresis loop generated during repeated heating and cooling cycles. A fully cured material has identical heating and cooling curves.

The first preimpregnated material selected for analysis was an epoxy prepreg, Trevarno F161.[1] Three cure cycles are given for this material, one for inspection, one for manufacturing, and one suggested by the prepreger. The cycle chosen by manufacturing was developed by trial and error and bears little resemblance to the other two. Gel time determined from Audrey data was close to that obtained by a standard technique.

Dissipation versus time and temperature curves are given. Using these curves it is possible to estimate the gel time of the prepreg, observe the dissociation temperature of the boron

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[1]Hexcel Corporation, Coast Manufacturing Division

trifluoride-monoethylamine complex that catalyzes the reaction, determine the point of pressure application in order to obtain a laminate with a specific resin content, and to determine a suitable cure schedule. In addition, with the Audrey data as a guide, aging becomes important only as it affects the physical properties of the final laminate and where the pressure required to induce flow is beyond equipment capabilities.

Although the potential of the equipment was verified, additional study will be required before the use of an Audrey·II dielectrometer can be incorporated into a materials standard or process traveler. The conclusions drawn from dielectric analysis require verification using conventional techniques such as physical properties tests and studying the chemistry of the preimpregnated material.

DISCUSSION

SCOPE AND PURPOSE

This work was done under PDO 6989221, Evaluation of F161 Prepreg using the Audrey II Dielectric Analyzer. The objective of this endeavor was to conduct an aging and process optimization study of Trevarno F161, an epoxy preimpregnated material and thereby evaluate the effectivity of the Audrey II dielectric analyzer[2] as a production and developmental tool. If successful, the study was to be used to supply data for an update of the materials standard and for process improvements designed to lower the scrap rate of production parts made from this material.

ACTIVITY

Testing Requirements

Probably some of the most difficult materials to characterize by conventional physical means are prepregs; cloth, mat, or strands of fiber that have been coated or preimpregnated with a resin/catalyst mixture and are then partially cured (B-staged) to provide limited room temperature stability. Prepregs exist in a fragile state of partial cure and are extremely sensitive to external stimuli. During storage the resin and catalyst continue to react, albeit slowly, so that the handling characteristics are constantly changing. Careless handling or improper storage accelerates these changes. To compensate for this condition the cure cycles recommended by the manufacturers are made deliberately vague. This allows the processor considerable flexibility in the choice of cure time, temperature, and pressure. Unfortunately, this reduces both receiving inspection and processing to a trial and error situation. Frequently material that is unacceptable by the more rigid criteria used by the receiving inspection department can be used to produce quality parts by modifying the production process.

The reverse is occasionally true; acceptable material can be unworkable for a specific application. In addition a production department may scrap dozens of parts before a suitable process can be developed by trial and error. Because of rising material and labor costs, procurement problems, and the inability of existing tests to indicate material quality, a technique was needed whereby both quality and processability could be determined.

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[2]Tetrahedron Associates, Incorporated

There are a variety of methods for determining the degree of cure and extent of crosslinking of a polymer, ranging from chemical analysis to heat distortion temperature (HDT) testing. Unfortunately the common chemical and mechanical tests usually require special specimen configurations and may also be destructive. This increases the difficulty of correlating laboratory results and processing problems. Dielectric analysis should be more satisfactory because the test is nondestructive and does not require a specially shaped specimen.

Quite simply, dielectric analysis is based on the intrinsic dielectric response of a polymeric material; this is the reaction of the dipoles within a polymer to an alternating electric field. These dipoles may be created artificially by charges collecting on anomalies within the material (interfacial polarization) or by unbalanced charge distribution within the molecule (orientational polarization). In either case the dipoles attempt to align themselves with the electric field. As the field alternates the dipoles attempt to swivel in step but are restricted because of their relatively fixed position within the polymeric structure. Capacitance can be described as a measure of the ability to align whereas dissipation is the power lost in alignment attempts. Thus the current leads the voltage and is attenuated. Both the dissipation and capacitance of a polymer are affected by viscosity, molecular weight, and the frequency of the alternating field. Molecular weight and viscosity relate directly to restricted dipole movement. If the frequency of the alternating field is too high, the dipoles within the material cannot move fast enough to respond to the changing field. Thermoplastic polymers have the simplest response patterns since the primary changes in these materials are caused by the effect of temperature on viscosity or thermal degradation on molecular weight. Thermosets have more complex responses because of the irreversible changes that take place during cure. Dipoles are created and disappear at the same time that viscosity and molecular weight are changing.

Testing Methods

The equipment selected for monitoring the dielectric responses of polymers was the Audrey II, System 300 dielectric analyzer (Figure 1). The System 300 package consists of the Audrey II, the ATC-200 temperature controller, a Research Incorporated, Model 5310 Data-Trak card reader, the Di/An 300 test cell and a modified Hewlett Packard RS-360 recorder. A Hewlett Packard 7044-A recorder, an oscilloscope, and a Carver[3] 12-ton (106.8 kN) laboratory press have also been added.

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[3]Fred S. Carver, Incorporated

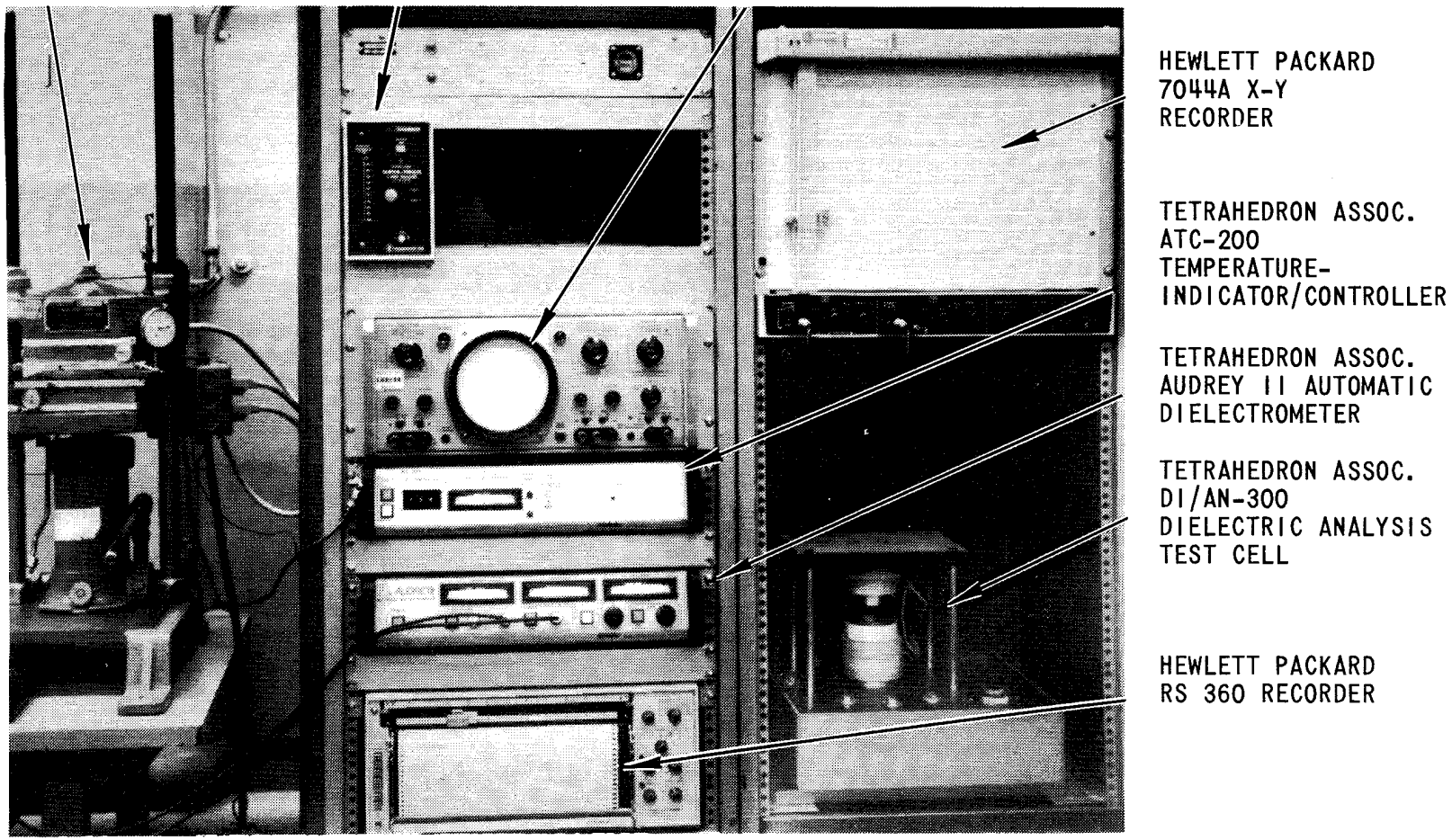

Figure 1. Equipment for Dielectric Analysis

In order to accommodate the variety of polymeric materials, three different electrode designs may be used with the Audrey II; the capacitive pair, the indirect electrode, and the Monoprobe. The capacitive pair, shown in Figure 2 is the most commonly used and can be disposable or permanent. If the material contains conductive reinforcement or cannot be placed between the capacitive pair electrodes, indirect electrodes similar to those in Figure 3 can be used. What little resin wicks up through the breather cloth during heat and pressure application is adequate for monitoring.

The Monoprobe, a capacitive pair in which one of the electrodes is electrical ground, simplifies the incorporation of electrodes within molds or where alignment of two electrodes would be difficult. It is particularly suited for monitoring continuous or batch type polymer cooks. One drawback is that the probe will seek ground through any available dielectric media so that external conditions may overshadow changes in the sample. A typical Monoprobe arrangement is shown (Figure 4).

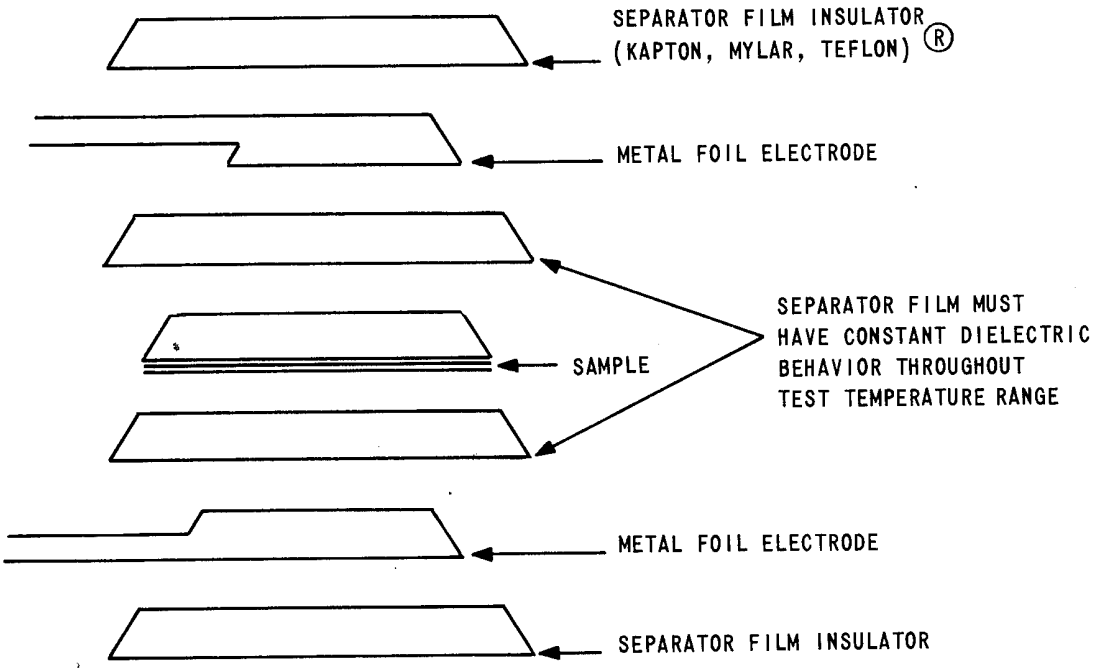

Figure 2. Capacitive Pair Electrodes

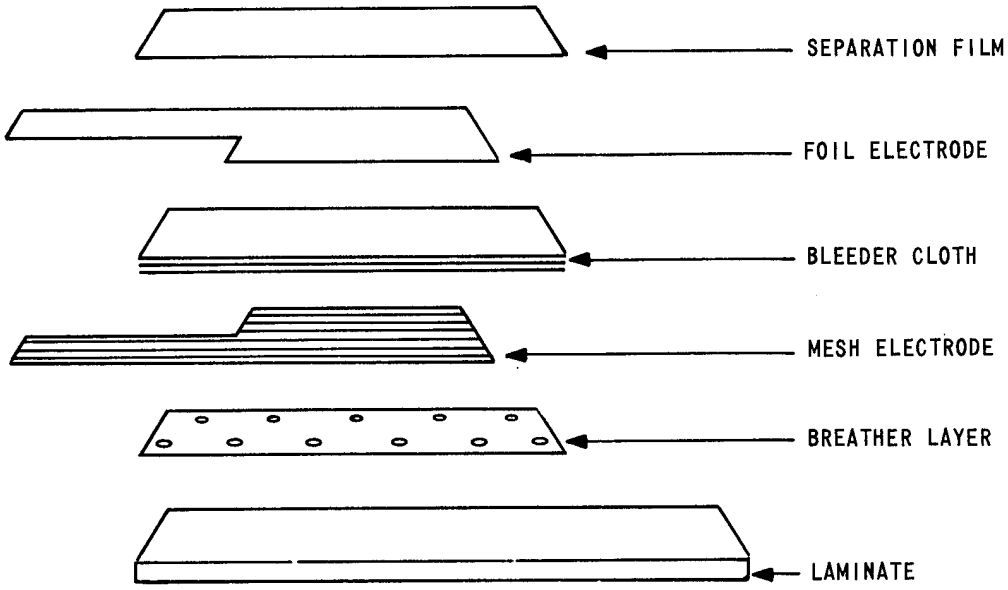

Figure 3. Indirect Electrodes

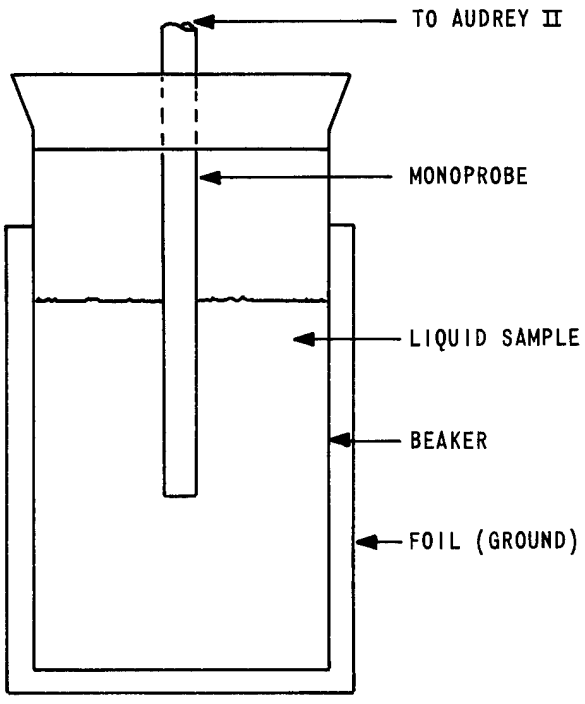

Figure 4. Monoprobe Setup

The Di/An/300 test cell contains a built in capacitive pair and is designed for low pressure tests. It was enhanced by the addition of the laboratory press, both of which can be controlled by the ATC-200 temperature controller assisted by the Data-Trak 5310, a card-type programmer. The oscilloscope provides a visual display of phase angle (dissipation is the tangent of the phase angle). Two recorders are used to simplify data handling. One provides dissipation, capacitance, and temperature as a function of time, and the other gives dissipation or capacitance as a function of temperature. Although both dissipation and capacitance data are available most data interpretation involves only the dissipation curves.

For a thermoset, dissipation versus time curves provide an insight into the curing mechanism and can be correlated to known physical and chemical changes. These curves are ideal for processing guides. The dissipation versus temperature curves can be used to obtain extent of cure information. This is done by monitoring dissipation versus temperature during several heat-up and cool-down cycles. The resultant circle curves indicate if any additional dielectric changes have occurred. If a material is fully cured at a given temperature no additional changes can take place and heat-up and cool-down curves will be identical. However, if the material is heated above its initial cure temperature, additional cure or thermal degradation will occur which will alter the cool-down portion of the cycle and subsequent cycles. Using the circle curves as a guide it should be possible to predict cure schedules without extensive physical properties testing.

The first prepreg selected for Audrey analysis was Trevarno F161 prepreg[4] (MS 2141289). The resin is an epoxy-Novolac similar to DEN 438[4] and is used to provide heat resistance to 500°F (260°C). The catalyst is a Lewis acid, boron trifluoride (BF_3). In itself BF_3 cures rapidly so for prepregs the reactivity is blocked by complexing with an amine, monoethylamine (MEA). The BF_3-MEA complex provides latency at room temperature while giving rapid cures above 195°F (90°C) where the complex dissociates. The resin catalyst mixture is prepreged onto a 181 style, Volan A (E. I. du Pont de Nemours and Company) treated fiberglass cloth. It is a low pressure laminating system certified to Mil-R-9300 and Mil-P-25421.

Three cure schedules are given in Appendix A. The first is recommended by Hexcel, the second is the one used to prepare test laminates for receiving inspection, while the third is a condensed version of the one used in production. The first two cycles are

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[4]Dow Chemical Company

similar except for the cure and postcure temperature. These were changed because of the nonproductive nature of a postcure temperature below that of the initial cure. The production cycle is considerably different. It was contrived in order to accommodate the 310°F (154°C) maximum operating temperature of the steam-heated press and to avoid changing the mold temperature. It is obvious from this comparison that any correlation between a quality test laminate and quality product is almost accidental and also indicates the problem with trial and error processing.

At present, acceptance testing consists of determining resin content for the prepreg, flow, tensile strength, flexural strength, and flexural modulus. Shelf life retest consists of checking tack and compressive properties. Flow, tack, and resin content are internal tests and are supposed to indicate processability.

All material used in this evaluation met the requirements of flow, tack, and resin content. Another test that can be used is gel time (MS 2141384-394). This gel time test is typical of most procedures used to analyze preimpregnated materials. The test is unscientific but it can be very useful since the cloth interferes with more traditional gellation tests. A resin bead is formed by squeezing the resin from a quantity of prepreg placed between the preheated platens of a press. The resin bead is then probed with a wooden stick (toothpick) to determine the point at which "stringiness" develops. The point at which long strings develop is considered to be the gel point. Obviously, this test is highly operator dependent. Gel time using this technique was run for comparison with the curves obtained from the Audrey analyzer. Both tests were conducted in the laboratory press. The results are given in Table 1. The specimen used in the Audrey analysis consisted of 4 plys of 4 by 4 inch (102 mm) squares of prepreg. The Audrey electrode size was 1.5 by 1.5 (38.2 mm) inches. Graphical representations of the dissipation versus time curves are given in Figures 5, 6, and 7. Since the dissipation is set on non-linear, all values are relative and are reported as chart divisions. Also, in order to magnify the results, the zero point of the recorder was moved up three chart divisions. Resolution was improved but it also became apparent that negative dissipations were occurring. Negative dissipation corresponds to power gain and suggests that an anomaly exists within the system. According to Stanley Yalof,[5] some materials do normally show negative dissipations and, although the exact cause is unknown, he feels the negative values are related to the interaction between the film layers and interfaces between the electrodes. The 250°F (121°C) curve is unique but once the temperature exceeds 300°F (149°C) the other curves are merely compressed versions of the

[5]Tetrahedron Associates, Incorporated.

Table 1. Gel Time Evaluation

2141384-94 Gel Time (minutes)	Audrey Gel Time (minutes)	Temperature (°F)	(°C)
35 ±5	11.5	250	121
4.2 ±0.4	4.4	300	149
2.5 ±0.2	3.0	325	163
1.5 ±0.2	1.5	350	179
1.0 ±0.2	1.1	370	188
	0.1	400	204

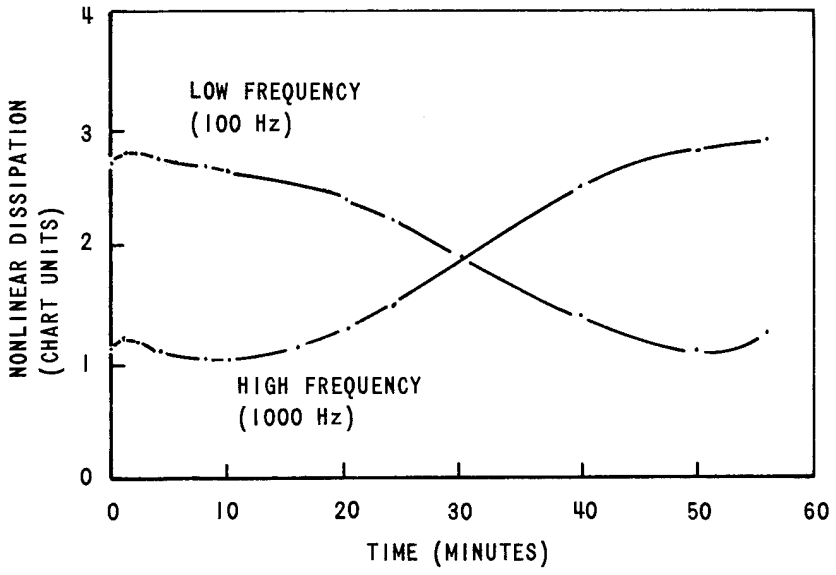

Figure 5. Dissipation as a Function of Time at 250°F (121°C) for Trevarno F161 Epoxy Preimpregnated Material Using Contact Pressure

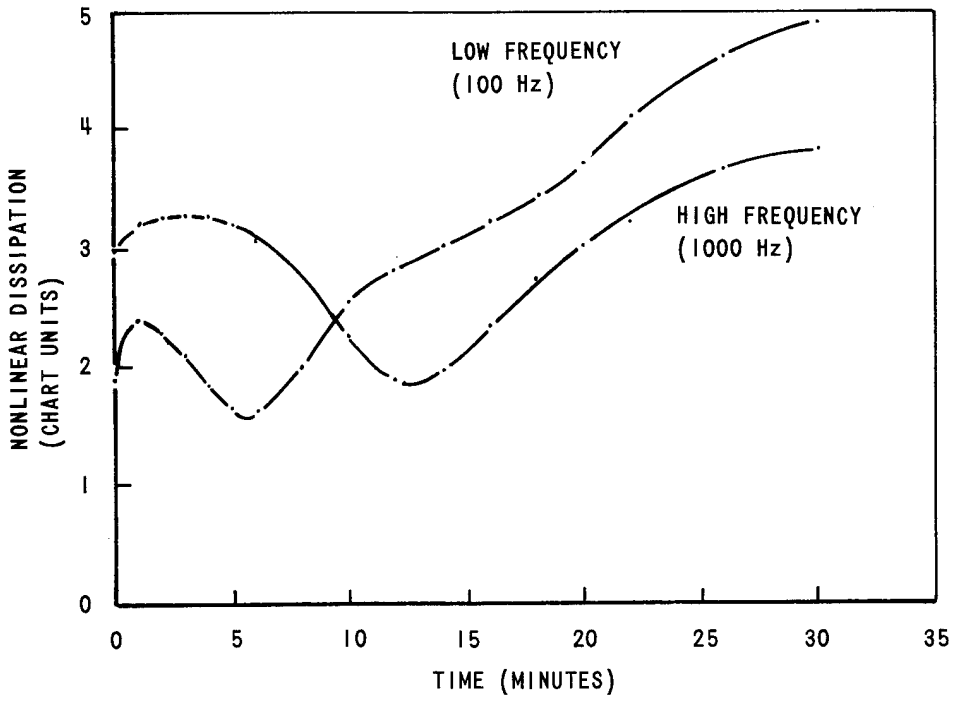

Figure 6. Dissipation as a Function of Time at 300°F (149°C) for Trevarno F161 Epoxy Preimpregnated Material Using Contact Pressure

300°F (149°C) curve. An examination of the 300°F (149°C) curve is useful to understand the data that has been gathered. According to the literature,[6] the first peak is related to how tightly the molecules are interconnected and is called the dispersion peak. It was anticipated that the molecules in this region would respond better at low frequency (low dissipation) than high, and this proved to be the case.

After the dispersion peak, the dissipation falls off rapidly. This occurs first for the low frequency range because the molecules require less energy (heat) to move. This is the period of softening and flow caused by decreasing viscosity. If contact pressure is maintained throughout the cycle flow caused by the viscosity, reduction would be from 2.5 to 4 percent. The 2.5 percent flow corresponds to the 250°F (121°C) cure while above 300°F (149°C) the flow is relatively constant at 4 percent.

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[6]Operating and Service Manual--Audrey II Dielectric Analyzer, Tetrahedron Associates, Incorporated.

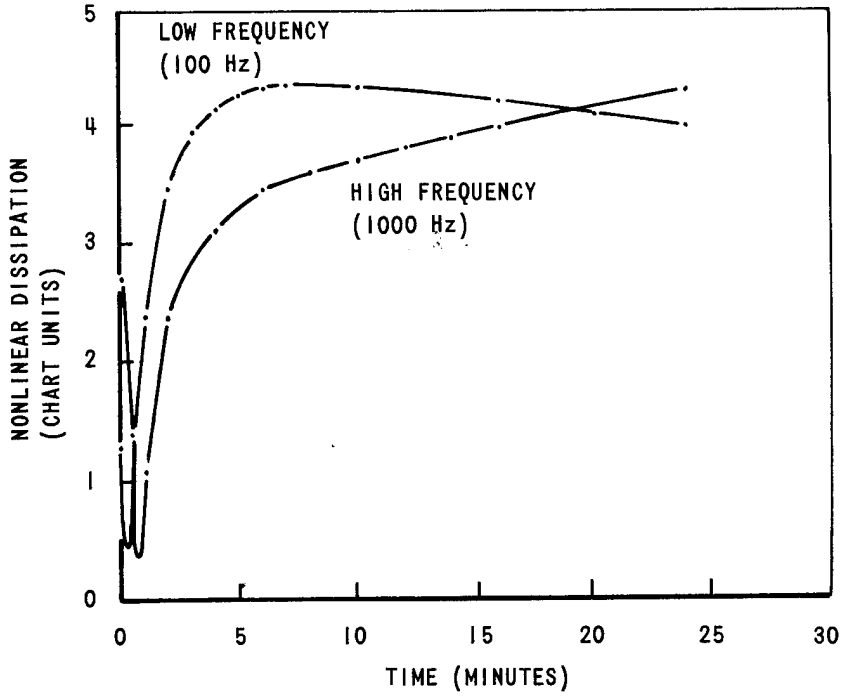

Figure 7. Dissipation as a Function of Time at 400°F (204°C) for Trevarno F161 Epoxy Preimpregnated Material Using Contact Pressure

For this prepreg, gellation is initiated at the minimum dissipation for the low frequency. This corresponds to the observed gellation values for all but the 250°F (121°C) curves. Until the second peak is reached, additional pressure will still cause the resin to flow, but the further the material progresses along this curve, the more pressure is required to cause flow. One interesting point in this upward curve is where the dissipation values for 100 and 1,000 Hz are equivalent. This is the point of zero flow at contact pressure and for the 250°F (121°C) curve also approximates the recorded gel time.

Once the second peak is reached, gellation of the material is essentially complete at that temperature although curing will continue. Exposure to higher temperature may result in a further period of softening and flow and can cause additional changes in dielectric response either by additional cure or degradation.

From the literature[7] we know that exotherm is a problem in a BF_3-MEA/DGEBA (epoxy resin) system; therefore, the recommended technique is to gel the system at 248°F (120°C) and follow with a postcure. This suggested cure is justified by the anomalous behavior recorded at 250°F (121°C) by the Audrey. At 250°F the reaction is sluggish and gellation proceeds slowly. Also there is little evidence of exotherm such as the rapid reduction in viscosity or gel time that is seen as the cure temperature increases from 300°F (149°C) to 400°F (204°C).

One of the problems with a sample that is only 4-plies thick is that it heats up too quickly and resolution in the heat-up phase is lost. Dissipation versus temperature curves allow for closer observation of this region as well as providing extent of cure information. Figure 8 shows a representative curve for F161 prepreg.

Key points are somewhat altered but still lend themselves to interpretation. At room temperature the power loss is higher at low frequency than at high frequency. This phenomenon may be related to the portion of the molecular structure that is trying to move. The whole chain may be flexing at low frequency whereas only the dipole is moving at higher frequencies.

As before, the dissipation peaks at a lower temperature for the low frequency curve and the downward trend corresponds to changing viscosity. The minimum point on the 100 Hz curve roughly approximates the dissociation temperature, 194°F (90°C), of the BF_3-MEA complex and the point where gellation begins. The area represented by the two frequency crossovers is not clearly understood. This change also occurs when material is put into a preheated press but is masked by the rapid heat-up. Possible contributors to this area include exotherm, chain extension, and intermediate ion formation. Further chemical study would be necessary to pinpoint responsibility. However, by using the 1,000 Hz cycle curve, the classic area of pressure application would be from about 230°F (110°C) upward; the point chosen depending on the amount of pressure available and the desired flow.

Another desirable product of plotting dissipation versus temperature is the circle curve used to predict extent of cure. Figure 9 is a circle curve for F161 prepreg using only the 1,000 Hz data. During the hour that this material cured at 325°F (163°C), the dissipation rose 3.5 chart divisions and then fell 0.5 division

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[7]H. Lee and K. Neville, *Handbook of Epoxy Resins*. New York: McGraw-Hill Book Company.

indicating that a cure did take place during that time. During cool-down the dissipation declines and then levels off. The second heat-up/cool-down cycle shows that the four plies of material are not fully cured at 325°F (162°C) after 60 minutes. The third heat-up curve is substantially closer to the second cool-down curve indicating that thermal cycling is advancing the cure and that complete cure can be shown using this technique. Increasing the temperature to 400°F (204°C) shows that additional cure also takes place during the high temperature portion of the post cure and that this sample, although not fully cured after one hour at 400°F (204°C) is rapidly approaching complete cure. Similar readings were taken using 10-ply laminate, except that even longer cure times were required to reach the same degree of cure. The Audrey takes the guesswork out of modifying the cure schedules recommended by the prepreger to suit an individual application.

When this project was proposed, the focus was to study aging and process optimization. However, during the course of the work it became apparent that with the Audrey as a guide, aging was important only as it affects the physical properties of the final laminate, and where the pressure required to induce the appropriate amount of flow is beyond the capabilities of production equipment.

Thus, the main area of concern is process optimization and we have shown that the Audrey is capable of performing this optimization. No actual optimization was attempted because of time and cost factors.

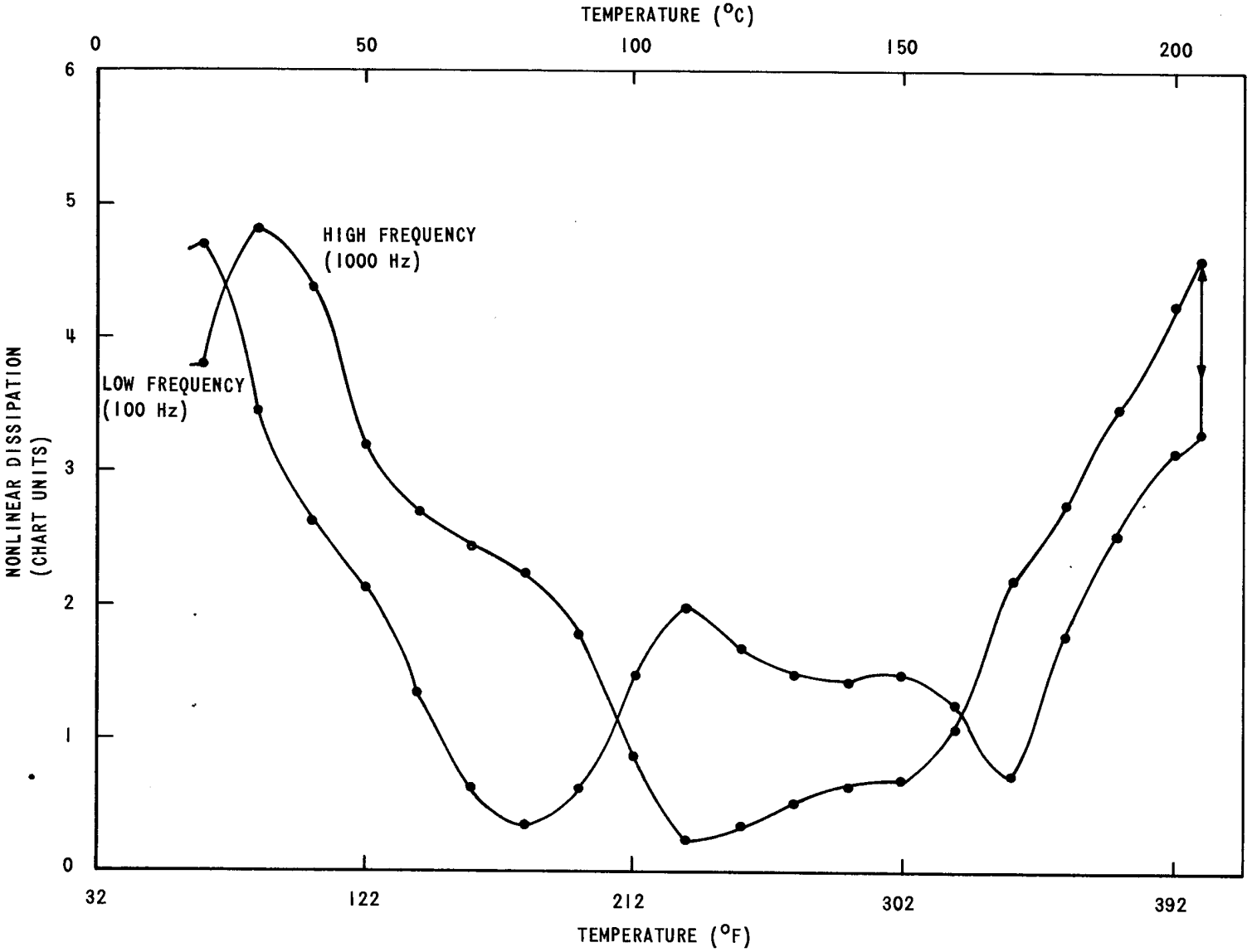

Figure 8. Dissipation as a Function of Temperature for Trevarno F161 Epoxy Preimpregnated Material Using Contact Pressure

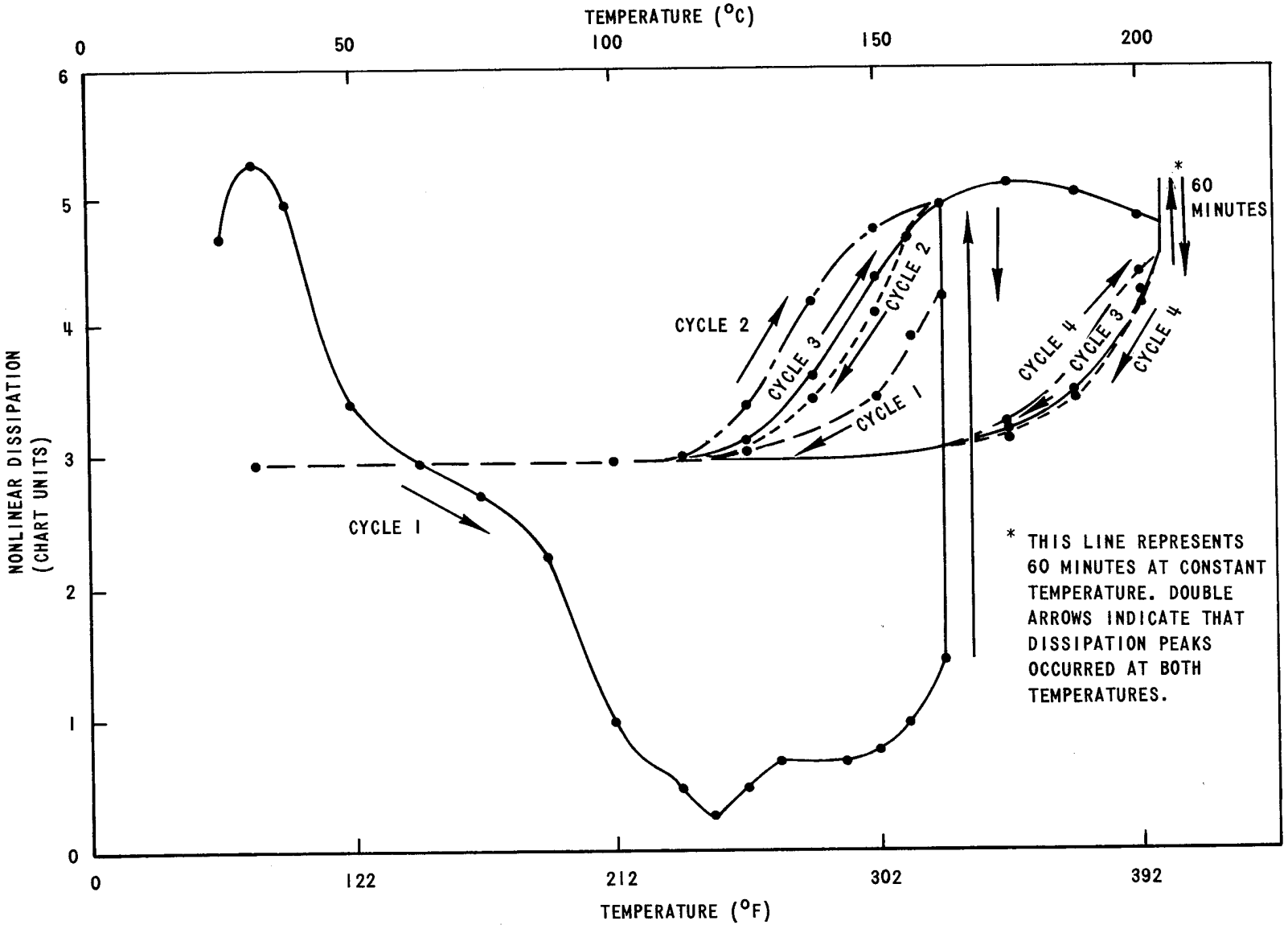

Figure 9. Dissipation as a Function of Temperature, Circle Curve for Trevarno F161 Epoxy Preimpregnated Material

ACCOMPLISHMENTS

Although the potential of dielectric analysis using the Audrey II dielectrometer was confirmed, the test results caused some modifications in the original goals. The aging portion of this investigation was not completed because the data suggest that the effects of aging on processability can be minimized if sufficient processing information via dielectric analysis is available.

The process optimization portion was considerably more successful. Dielectric analysis pointed out the chemical basis for the manufacturer's cure cycle, showed areas where improvements could be made and indicated how far away from these basic material requirements trial and error processing could lead.

The key to dielectric analysis is data interpretation. Physical properties data and a knowledge of the chemistry of the system being analyzed are used in conjunction with dielectric behavior. This makes incorporation of this test into a rigid format such as a materials standard or process traveler considerably more difficult than was previously supposed. Additional work, beyond the limited scope of a short term PDO, will be required to fully develop the interface between dielectric behavior and process control.

Appendix A

PRESS CURE CYCLES

Appendix A

PRESS CURE CYCLES

Hexcel's Recommended Cycle[1]

Cure temperature and time	1.5 hours at 325°F (163°C)
Cure pressure	50 to 200 psi (0.345 to 1.37 MPa)
Number of plies	12 to 13 (nested)
Postcure	2 hours at 300°F (149°C) plus 3 hours at 400°F (204°C)

Introduce part to press platens preheated to 250°C (121°C). Apply a contact pressure of 15 to 20 psi (0.103 to 0.137 MPa) for 2 to 3 minutes, and then bump the part several times by releasing and reapplying the contact pressure. After 15 to 20 minutes at 250°F apply full laminating pressure of 100 to 200 psi (0.689 to 1.37 MPa) and then raise the temperature to 325°F (163°C). Cure the part at 325°F for 1.5 hours.

Receiving Inspection Cycle

Cure temperature and time	1.5 hours at 300°F (149°C)
Cure pressure	200 psi (1.37 MPa)
Number of plies	15 (nested)
Postcure	2 hours at 300°F (149°C) plus 2 hours at 400°F (204°C)

Introduce part to press platens preheated to 250°F (121°C). Apply contact pressure for 2.5 minutes. Bump 5 times and hold an additional 15 minutes at 250°F (121°C). Increase pressure to 25 psi (0.172 MPa) and the temperature to 300°F (149°C). Cure for 1.5 hours and cool under pressure.

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[1]Hexcel Corporation, Coast Manufacturing Division, D. B. Number 805, April 1, 1970

Production Cycle

1. Lay up preforms at 135 to 150°F (57 to 66°C). Store below 45°F (7.2°C).

2. B-stage layups for 0 to 6 hours at 175°F (79.5°C). Store.

3. Preheat mold to 295 ±5°F (146 ±2.8°C). Remove layup from cooler and allow to stabilize 3 to 8 hours before using.

4. Advance mold to 0.0625 inch (1.58 mm) from close and allow 2.5 minutes ±55 seconds for B-stage. Close press and cure for 25 minutes at 295°F (146°C) and 150 to 200 tons (136 to 181 Mg) clamp pressure. Postcure for 1 hour at 390°F (199°C). After machining postcure an additional 2 hours and 55 minutes at 390°F (199°C). If part is out of tolerance heat to 400°F (204°C) for 10 minutes and place on a preheated 170°F (77°C) cooling fixture.

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